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chemical resistance test and the laundering test. Reference may be made to Bureau of Engraving standard test methods 300.002, 300.004, and 300.005.

As used in this invention:

"High melt strength polypropylene" refers to homo- and copolymers containing 50 weight percent or more propylene monomer units, and having a melt strength in the range of 25 (0.25 N) to 60 cN (0.60 N) at 190°C.

"Ink receptive" means a coating, treatment or layer which that is wetted by the ink and the ink adheres thereto.

Alpha-transition temperature,  $T_{\alpha}$ , means to the temperature at which crystallite subunits of a polymer are capable of being moved within the larger lamellar crystal unit. Above this temperature lamellar slip can occur, and extended chain crystals form, with the effect that the degree of crystallinity is increased as amorphous regions of the polymer are drawn into the lamellar crystal structure.

"Security document" means a document that might be prone to counterfeiting, and may be taken from, but not limited to the following example: currency, stock and bond certificates, birth and death certificates, automobile titles, land titles and abstracts and the like.

"Small-cell foam" means a foam having average cell dimensions of less than 100 micrometers ( $\mu\text{m}$ ), preferably 5 to 50  $\mu\text{m}$  (prior to orientation);

"closed-cell" means a foam that contains substantially no connected cell pathways that extend from one outer surface through the material to another outer surface;

"operating temperature" means the temperature that must be achieved in the extrusion process to melt all of the polymeric materials in the melt mix;

"exit temperature" and "exit pressure" mean the temperature and pressure of the extrudate in the final zone or zones of the extruder;

"melt solution" or "melt mixture" or "melt mix" means a melt-blended mixture of polymeric material(s), any desired additives, and blowing agent(s) wherein the mixture is sufficiently fluid to be processed through an extruder;

"neat polymer" means a polymer that contains small amounts of typical heat-stabilizing additives, but contains no fillers, pigments or other colorants, blowing agents, slip agents, anti-blocking agents, lubricants, plasticizers, processing aids, antistatic agents, ultraviolet-light stabilizing agents, or other property modifiers;

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The ink-receptive substrate may be prepared by the steps of:

- (1) providing an oriented, high melt-strength polypropylene foam, and
- (2) providing an ink-receptive surface on at least one major surface of the foam, wherein the ink-receptive surface may comprise a surface treatment, such as corona or flame treatment, an ink-receptive coating, or a film layer that is inherently ink-receptive.

The oriented, high melt-strength polypropylene foam may be prepared by the steps of:

- (1) mixing at least one high melt strength polypropylene and at least one blowing agent in an apparatus having an exit shaping orifice at a temperature and pressure sufficient to form a melt mixture wherein the blowing agent is uniformly distributed throughout the polypropylene;
- (2) reducing the temperature of the melt mixture at the exit of the apparatus to an exit temperature that is no more than 30°C above the melt temperature of the neat polypropylene while maintaining the melt mixture at a pressure sufficient to prevent foaming;
- (3) passing the mixture through said exit shaping orifice and exposing the mixture to atmospheric pressure, whereby the blowing agent expands causing cell formation resulting in foam formation, and
- (4) orienting said foam.

The oriented, high melt-strength polypropylene foam may be prepared by using a foamable mixture comprising a major amount of a high melt-strength polypropylene and a minor amount of second polymer component comprising a semicrystalline or amorphous thermoplastic polymer. Polymer mixtures comprising a high melt-strength polypropylene and two or more added polymers are also within the scope of the invention.

The high melt strength polypropylene useful in the present invention includes homo- and copolymers containing 50 weight percent or more propylene monomer units, preferably at least 70 weight percent, and has a melt strength in the range of 25 (0.25 N) to 60 cN (0.60 N) at 190°C. Melt strength may be conveniently measured using an extensional rheometer by extruding the polymer through a 2.1 mm diameter capillary having a length of 41.9 mm at 190°C and at a rate of 0.030 cc/sec; the strand is then

stretched at a constant rate while measuring the force to stretch at a particular elongation. Preferably the melt strength of the polypropylene is in the range of 30 (0.30 N) to 55 cN (0.55 N), as described in WO 99/61520.

The melt strength of linear or straight chain polymers, such as conventional isotactic polypropylene, decreases rapidly with temperature. In contrast, the melt strength of highly branched polypropylenes does not decrease rapidly with temperature. It is generally believed that the differences in melt strengths and extensional viscosity is attributable to the presence of long chain branching. Useful polypropylene resins are those that are branched or crosslinked. Such high melt strength polypropylenes may be prepared by methods generally known in the art. Reference may be made to U.S. 4,916,198 (Scheve et al) which describes a high melt strength polypropylene having a strain-hardening elongational viscosity prepared by irradiation of linear propylene in a controlled oxygen environment. Other useful methods include those in which compounds are added to the molten polypropylene to introduce branching and/or crosslinking such as those methods described in U.S. 4,714,716 (Park), WO 99/36466 (Moad, et al.) and WO 00/00520 (Borve et al.). High melt strength polypropylene may also be prepared by irradiation of the resin as described in U.S. 5,605,936 (Denicola et al.). Still other useful methods include forming a bimodal molecular weight distribution as described in J.I. Raukola, A New Technology To Manufacture Polypropylene Foam Sheet And Biaxially Oriented Foam Film, VTT Publications 361, Technical Research Center of Finland, 1998 and in U.S. 4,940,736 (Altepping and Nebe).

The foamable polypropylene may be comprised solely of propylene homopolymer or may comprise a copolymer having 50 wt% or more propylene monomer content. Further, the foamable propylene may comprise a mixture or blend of propylene homopolymers or copolymers with a homo- or copolymer other than propylene homo- or copolymers.

Particularly useful propylene copolymers are those of propylene and one or more non-propylenic monomers. Propylene copolymers include random, block, and grafted copolymers of propylene and olefin monomers selected from the group consisting of ethylene, C3-C8  $\alpha$ -olefins and C4-C10 dienes. Propylene copolymers may also include terpolymers of propylene and  $\alpha$ -olefins selected from the group consisting of C3-C8  $\alpha$ -olefins, wherein the  $\alpha$ -olefin content of such terpolymers is preferably less than 45 wt%.

substrate during nitrogen corona treatment should be above the glass transition temperature of the film but less than the melting point of the film, preferably at room temperature.

The preferred oxygen concentration, at the corona, for this process, is less than 200 ppm and most preferred less than 20 ppm. A side benefit of these low oxygen concentrations, is that no environmental control of emissions is necessary because of the low levels of  $\text{NO}_x$  and  $\text{O}_3$  produced.

Flame treatment can be carried out on any commercial gas flaming equipment known to those skilled in the art. Either high-velocity or ribbon burners may be used. The air:fuel ratio of the combustion mixture must be less than the stoichiometric ratio (typically 9.6 for air:natural gas mixtures) and preferably between 8.8 and 9.4 by volume. This air:fuel mixture produces a so-called "reducing" or "rich" flame. Although natural gas with an energy value of approximately 1000 BTU/ft<sup>3</sup> ( $3.5 \times 10^7 \text{ J/m}^3$ ) is the preferred fuel, other gaseous hydrocarbons such as acetylene, ethane, propane, butane, or liquefied petroleum gas (LPG) can also be used, provided that the air:fuel ratio is adjusted to less than stoichiometric. Although air is the preferred oxidizer, oxygen or oxygen-enriched air can be used, again provided that the air:fuel ratio is adjusted to less than stoichiometric.

The desired flow rate of fuel may be adjusted to provide the optimal thermal output for a given width, thickness, and processing speed of the polypropylene foam backing. The volume of gas burned should be 0.4-6.0 liters of natural gas per square meter of polypropylene foam to be flamed, and preferably between 0.6-1.5 liters of natural gas/m<sup>2</sup> polypropylene foam. Exposure times to the flame should be between 0.001-0.05 seconds to prevent thermal damage to the polypropylene foam.

Flame treating equipment that may be suitable in some applications is commercially available from Flynn Burner Corporation of New Rochelle New York, USA, The Aerogon Company Ltd. of Alton, United Kingdom; and Sherman Treaters Ltd. of Thame, United Kingdom. Corona treating equipment which may be suitable in some applications is commercially available from Enercon Industries Corporation of Menomonee Falls, Wisconsin, USA; Pillar Technologies of Hartland, Wisconsin, USA; and Corotec Corporation of Farmington, Connecticut, USA.

When using an ink-receptive coating on an oriented foam substrate, the ink receptive layer has a weight of between about 0.5 and about 250 g/m<sup>2</sup>. In a preferred

at 5.5 lbs/hr (2.3 kg/h) using a Killion 2.5 cm single screw extruder (Davis-Standard Corp., Cedar Grove, NJ). The combined streams were then fed into the core of a 254 mm three-layer die set at 182°C. The outside layers of the die were not used. The resulting foam sheet with skins was cooled on a chrome cast roll at 10°C, then collected at a draw rate of 3.3 m/min. The foam composite had a density of 0.56 g/cc at a thickness of 1.24 mm.

This foam was biaxially oriented using a Karo batch orienter at draw ratios of 4 in the machine direction (MD) and 4 in the cross direction (CD). The temperature during orientation was 140°C. The density of the oriented foam composite was 0.25 g/cc. The oriented foam was opaque and still had a paper-like feel since the skin thickness was less than the cell size of the foam. This foam was subjected to the Printability/Ink Adhesion, Launderability, and Crumple Evaluation tests as described above and then rated for ink adhesion. The sample rated a 1 in the unscored, scored, and crumple tests, and rated a 2 in the launderability test.

#### Example 16

The foam of Example 5 was treated with a nitrogen corona of 1 J/cm<sup>2</sup> on both sides. The surface-treated foam was then extrusion-coated with Bynel 3101 on one side to create a 2-layer foam/unfoamed skin composite. The Bynel 3101 was fed into a 254 mm, single-layer die using a 1.9 cm single-screw Killion extruder (Davis-Standard Corp., Cedar Grove, NJ). The temperature profile of the extruder went from 380 to 440°C and the die was set at 440°C. The Bynel 3101 was fed at 5.3 lb/hr and the coated foam was collected at a draw rate of 12.2 m/min. The coated side of the foam was tested according to the Printability/Ink Adhesion test described above and rated a 1 in both the unscored and scored tests.

Table 1

## Claims:

1. A printable substrate comprising at least one high melt-strength, oriented polypropylene foam layer having an ink-receptive surface.
2. The substrate of claim 1 wherein the high melt-strength polymer has a melt strength of of 25 (0.25 N) to 60 cN (0.60 N) at 190°C.
3. The substrate of claim 1 wherein said orientation is biaxial.
4. The substrate of claim 1 wherein said polymer is a high melt-strength polypropylene comprising homo- and copolymers containing 50 weight percent or more propylene monomer units.
5. The substrate of claim 4 wherein said polypropylene copolymers are selected from random, block, and grafted copolymers of propylene and an  $\alpha$ -olefin selected from the group consisting of C3-C8  $\alpha$ -olefins and C4-C10 dienes.
6. The substrate of claim 1 wherein said high melt strength polypropylene comprises a blend of a major amount of said high melt strength polypropylene and a minor amount of another semicrystalline or amorphous polymer.
7. The substrate of claim 1 wherein said high melt strength polypropylene further comprises an inorganic additive.
8. The substrate of claim 3 wherein said orientation is at least 9 X total draw ratio.
9. The substrate of claim 1 wherein said foam, prior to orientation, has an average cell dimension of 50 micrometers or less.
10. The substrate of claim 1 further comprising at least one thermoplastic film layer.

(2) reducing the temperature of the melt mixture at the exit of the apparatus to an exit temperature that is no more than 30°C above the melt temperature of the neat polypropylene while maintaining the melt mixture at a pressure sufficient to prevent foaming;

5 (3) passing the mixture through said exit shaping orifice and exposing the mixture to atmospheric pressure, whereby the blowing agent expands causing cell formation resulting in foam formation, and

(4) orienting said foam.

10 39. The process of claim 37 wherein said foam is biaxially oriented.

40. The process of claim 39 wherein said orientation is at or above the alpha transition temperature and below the melt temperature of the polypropylene.

15 41. The process of claim 39 wherein said orientation is simultaneous biaxial.

42. The process of claim 37 wherein said high melt-strength polypropylene comprises homo- and copolymers containing 50 weight percent or more propylene monomer units, and having a melt strength in the range of 25 (0.25 N) to 60 cN (0.60 N) at 190°C.

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43. The process of claim 42 wherein said polypropylene copolymers are selected from random, block, and grafted copolymers of propylene and an  $\alpha$ -olefin selected from the group consisting of C3-C8  $\alpha$ -olefins and C4-C10 dienes.

25 44. The process of claim 37 wherein said mixture comprises a blowing agent and a blend of a major amount of a high melt strength polypropylene and a minor amount of a semicrystalline or amorphous polymer.

45. The process of claim 37 wherein said extruding step comprises extruding said  
30 mixture at a pressure  $\geq 2500$  psi (17.2 Mpa).

46. The process of claim 41 wherein said orientation is 3 to 70x total draw ratio.



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